HIGH CONDUCTIVITY BARE ALUMINUM FINSTOCK AND RELATED PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/400,735, filed August 1, 2002, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates to an alloy composition and to a method for fabricating finstock, more particularly, the invention relates to an aluminum alloy composition and method for fabrication of finstock for applications such as aluminum heat exchanger end uses.

Description of Related Art

[0003] Bare finstock for brazed automotive aluminum heat exchangers is typically fabricated from 3XXX Series aluminum alloys such as AA3003 aluminum, an Aluminum Association ("AA") alloy designation. After brazing, these alloys are characterized by relatively low thermal conductivity as measured by electrical conductivity ("EC") because of the high level of manganese trapped in solid solution in these alloys. Since the fins of such heat exchangers need to conduct heat away from the fluid carrying tubes, the thermal conductivity of these fins will impact the overall efficiency of the heat exchangers into which they are installed.

[0004] As heat exchanger fabricators endeavor to reduce the weight of components, downgauging of the tubes and fins becomes necessary. Given existing designs of automotive heat exchangers, downgauging the fin requires an increase in conductivity, while still maintaining some minimum level of post-braze strength and self-corrosion resistance, if the efficiency and lifetime of the component is not to be compromised.

[0005] In an effort to produce such finstock, compositions and processes have been modified. A typical example of the foregoing is disclosed in U.S. Patent Nos. 6,592,688, 6,165,291, 6,238,497, 5,217,547, U.S. Publication No. 2003/0015573 and European Application No. EP1156129.

[0006] U.S. Patent No. 6,238,497 describes a method of producing a high conductivity finstock. The method includes steps of continuously casting an aluminum alloy strip, rolling the as-cast strip to an intermediate gauge, annealing the intermediate gauge strip and then cold rolling to the final gauge. The alloy contains in wt.%: 1.6 to 2.4% Fe, 0.7 to 1.1% Si,

0.3 to 0.6% Mn, 0.3 to 2.0% Zn with 0.005 to 0.040% Ti optional. The solidification cooling rates specified in U.S. Patent No. 6,238,497 relate to continuous slab casting technologies as the initial step in fabricating the finstock.

[0007] In U.S. Patent No. 6,592,688 a high conductivity aluminum fin alloy is described as containing: 1.2 to 1.8% Fe, 0.7 to 0.95% Si, 0.3 to 0.5% Mn, 0.3 to 1.2% Zn with 0.005 to 0.02% Ti optional. The solidification cooling rates described in this patent also relate to slab casting technologies.

[0008] U.S. Patent No. 6,165,291 describes a process for fabricating an aluminum alloy fin with high post-braze conductivity. The process involves continuous strip casting the aluminum alloy, rolling it to an intermediate gauge, annealing the intermediate gauge strip and then cold rolling to final gauge. The alloy contains 1.2 to 2.4% Fe, 0.5 to 1.1% Si, 0.3 to 0.6% Mn, 0 to 1.0% Zn with 0.005 to 0.040% Ti optional. The patent indicates that Si is instrumental in developing strength through a combination of particle strengthening and solid solution strengthening and that below 0.5 wt.% Si there is insufficient Si for strengthening purposes. It is noted that the cooling rates described in this patent relate to twin roll casting technologies of aluminum alloys. It is further noted that twin roll casting technologies have been employed within the aluminum industry for years to produce common finstock alloys such as AA3003.

[0009] In view of the foregoing, there is a need for producing lighter weight finstock with efficient post-braze strength, conductivity and corrosion resistance.

SUMMARY OF THE INVENTION

[0010] Generally, the present invention is an aluminum alloy finstock composition that achieves improved post-braze strengths by a combination of particle and solute strengthening. In doing so, the present invention can achieve an attractive combination of post-braze ultimate tensile strength ("UTS") of roughly about 125MPa, with electrical conductivity values of about 48% IACS or greater and with good self-corrosion resistance. One preferred range for this alloy composition, suitable for a controlled atmosphere brazing ("CAB") with conventional fluxes that are not magnesium tolerant include: about 0.35–0.60 wt.% Si; about 1.8–2.6 wt.% Fe; about 0.02–0.30 wt.% Cu; about 0.40–0.70 wt.% Mn; up to about 3.0 wt.% Zn; up to about 0.05 wt.% In; and up to about 0.05 wt.% Ti, the balance being aluminum, incidental elements and impurities. The alloy may also include up to about 0.20 wt.% Zr; about 0.05 wt.% or less Mg and about 0.05 wt.% or less Ni. Preferably, the alloy includes 0.35 - 0.5 wt.% Si, more preferably about 0.35 - 0.45 wt.% Si. The alloy also preferably

includes about 1.8-2.4 wt.% Fe, about 0.4-0.7% Mn, about 0.15-0.25 wt.% Cu, up to about 0.15 wt.% Zn and about up to 0.03 wt.% In. When the alloy of the present invention is used in a controlled atmosphere braze with Mg tolerant fluxes, up to about 0.3 wt.% Mg may be tolerated with the aforesaid elemental ranges.

[0011] The present invention is also directed to a process of making aluminum alloy finstock having improved combinations of post-braze tensile strength, electrical conductivity and self-corrosion resistance. The process includes continuously casting into sheet an alloy with the composition described hereinabove into a sheet, rolling the sheet to an intermediate anneal gauge, annealing the rolled sheet, and cold rolling to a final desired gauge.

[0012] Continuous casting of the sheet may be performed with a twin roll caster under rapidly cooling casting conditions that substantially avoid the formation of primary intermetallic solidification compounds and produces a sheet of thickness of about 2.0-10.0 mm, preferably about 6.0 mm. The casting may be performed with a high speed sheet or belt caster that freezes from at least one surface to substantially avoid formation of primary intermetallic solidification compounds.

[0013] The step of rolling the sheet to an intermediate anneal gauge may include more than one intermediate thermal operation at either cast gauge or after some initial cold reduction. The thermal operation may include a 1-10 hour soak, preferably 1-8 hour soak, at a temperature range of about 320-450°C. Rolling may include both hot or warm rolling and cold rolling.

[0014] The rolled sheet may be annealed at a temperature below about 450°C. The step of cold rolling to a final gauge may produce less than or equal to about 50% reduction in sheet thickness.

[0015] The finstock alloy of the present invention provides enhanced post-braze conductivity of about 48% IACS or greater as compared to its AA3003 counterpart with values of about 41% IACS.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] When referring to any numerical range of values, such ranges are understood to include each and every number and/or fraction between the stated range minimum and maximum. A range of about 0.35-0.60 wt.% silicon, for example, would expressly include all intermediate values of about 0.36, 0.37, 0.38 and 0.40%, all the way up to and including 0.55, 0.57 and 0.59% Si. The same applies to each other numerical property, relative thickness and/or elemental range set forth herein.

[0017] The present invention is an aluminum alloy finstock composition that achieves improved post-braze strengths by a combination of particle and solute strengthening. In one embodiment, the alloy includes about 0.35-0.60 wt.% Si; about 1.8-2.6 wt.% Fe; about 0.02-0.30 Cu; about 0.40-0.70 wt.% Mn; up to about 3.0 wt.% Zn and up to about 0.05 wt.% In; and up to about 0.05 wt.% Ti, the balance being aluminum, incidental elements and impurities. Preferably, the alloy includes 0.35 - 0.5 wt.% Si, more preferably about 0.35 - 0.45 wt.% Si. The alloy also preferably includes about 1.8-2.4 wt.% Fe, about 0.4-0.7% Mn, about 0.15-0.25 wt.% Cu, up to about 0.15 wt.% Zn and about up to 0.03 wt.% In.

[0018] The alloy of the present invention includes about 0.35-0.60 wt.% Si, preferably 0.35-0.50 wt.% Si. Below 0.35 wt.% the strengthening effect of Si is expected to be minimal. Silicon contents greater than 0.50 wt.% may not be necessary for the combinations of properties of interest.

[0019] Iron is important in the formation of the small intermetallic particles during solidification. These particles are important for post-braze dispersion strengthening and for influencing the post-braze grain size. The Fe range is set at about 1.8-2.6 wt.%, preferably about 1.8-2.4 wt.%. Below 1.8 wt.% the strengthening effect is insufficient, whereas, above 2.6 wt.% it is difficult to cast the alloy without formation of coarse intermetallic Fe-bearing particles that would create a problem during the fabrication of thin gauge finstock.

[0020] Manganese is important in modifying the Fe-bearing intermetallic particles. Manganese will combine with the Fe and Si in the intermetallic particles and in so doing, increase the volume fraction of particles for strengthening. In addition, Mn will shift the corrosion potential of the intermetallic particles to make it closer to the matrix, thus reducing the self-corrosion rate. Finally, Mn in solution can contribute to solid solution strengthening, although at the detriment of conductivity. For these reasons, Mn is set to the range of about 0.40 - 0.70 wt.%. Below 0.40% the beneficial attributes of Mn are not fully realized, whereas, above 0.70% Mn the post-braze conductivity of the alloy is notably reduced.

[0021] Copper is important for solute strengthening. While copper is often avoided as an alloy addition to finstock for its effect on corrosion, the unexpected results of the present invention show that at the levels of Cu explored the self-corrosion rate of these alloys did not notably increase, whereas the post-braze strength was improved. For that reason, the range of Cu addition is set at 0.02-0.30 wt.%.

[0022] Zinc, if present, is added for purposes of making a fin less noble than the tube to which it is brazed thereby affording cathodic protection to the tube. Experimental work has

also indicated that the Zn is providing some additional solute strengthening. It has been observed that additions of zinc of greater than about 2.0 wt.% are generally not desirable. Such additions have a detrimental influence on conductivity and self-corrosion rates. In some instances, though, it may be necessary to sacrifice those properties to allow for sufficient cathodic protection of the tube. The maximum Zn limit of up to about 3.0 wt.% for this invention was established with that potential compromise in mind.

[0023] Indium is also a potential addition to shift the corrosion potential of the fin. Additions of about 0.017 wt.% In were found effective in combination with Zn additions to shift the potential with minimal influence on conductivity. In laboratory work, additions of 0.078 wt.% were found to result in notable increased self-corrosion rates so a range of 0 - 0.05 wt.% indium is established for this alloy. These additions are envisioned to be effective either without Zn additions or in combination with Zn additions.

[0024] Titanium is present for purposes of grain refinement during casting. For this reason Ti levels of up 0.05 wt.% are useful.

[0025] Zirconium, may be included for controlling the post-braze grain size and shape. However, it has a negative impact on conductivity. For this reason, Zr may not be present in the alloy, but additions of up to 0.2 wt.% are tolerable.

[0026] Magnesium is known to be an effective element from a strengthening standpoint. In alloys containing Si or where Si will be present due to diffusion from the Al-Si braze alloy during brazing, Mg can contribute to strengthening through precipitation hardening by Mg_2Si. Magnesium is preferably not present in CAB brazing alloys due to the detrimental influence of Mg on brazeability when using popular commercial fluxes (such as Nocolok®). Nevertheless, fluxes are being developed that are more tolerant of Mg and so the Mg limits for this alloy are set at 0 - 0.3 wt.%. For better CAB "braze-ability" with a conventional brazing flux, magnesium contents are kept purposefully low, less than about 0.05 wt.%. When a magnesium-tolerant flux is used, however, higher Mg levels of up to about 0.3 wt.% may be considered for additional strengthening. Such Mg amounts should be able to combine with the Si in solution after brazing to precipitate a Mg_2Si strengthening phase. In so doing, high conductivity is maintained by pulling the Mg and Si from solid solution.

[0027] The process of making the aluminum alloy finstock with the above-described composition includes the steps of continuously casting into a sheet, cold rolling, annealing and cold rolling the annealed sheet to a final gauge. Because of the high Fe content, the alloy of the present invention is preferably cast by a process that achieves very high cooling rates

(greater than about 200°C/sec) during solidification. Such high cooling rates assure the formation of small diameter intermetallic particles during freezing that fragment during subsequent thermo-mechanical processing, thus providing the large population of very small particles for dispersion strengthening. Twin roll casting is particularly well suited for this purpose. Alternatively, casting can be performed on a high speed continuous belt caster whose design affords high cooling rates. One such caster is described in U.S. Patent No. 5,564,491. "High speed belt casting", as used herein, refers to strip casting at speeds of greater than about 30 meters/minute. Alternative casting methodologies that should also suffice include "melt drag casting" and most high speed, twin roll strip casting processes that freeze the resultant strip product (from one or both sides) with sufficiently high cooling rates during solidification. The high speed sheet or belt caster processes freeze from at least one surface at rates sufficient to substantially avoid formation of primary intermetallic solidification compounds. These rates are known by one skilled in the art.

[0028] When the alloy of the present invention is twin roll cast to sheet, between about 2 to 8 mm thick, preferably it is cold rolled to an intermediate gauge in several rolling passes, annealed and then cold rolled to final gauge. For purposes of facilitating the cold rolling of strip, it may be advisable to include an additional intermediate thermal treatment immediately after casting, or after some initial cold roll reduction. The thermal operation may include a 1 - 10 hour soak preferably 1 - 8 hour soak at a temperature of about 320 - 450°C or about 370 - 450°C. This can be followed by additional cold rolling to a second, intermediate gauge, annealing and then cold rolling to final gauge. Total cumulative thermal exposures during strip processing may be limited to minimize the coarsening of intermetallic particles. Typically, one intermediate anneal is preferred.

[0029] For the scenarios that involve casting alloy strip on a high speed caster (either belt or twin roll), the initial rolling passes may be accomplished by a combination of hot and warm rolling to intermediate gauge after which an optional intermediate anneal may be appropriate. Thereafter, the sheet may be cold rolled to an inter-anneal gauge, before being annealed and cold rolled to final gauge. If the alloy of the present invention were to be cast on a melt drag apparatus, then the coil of same preferably is cold rolled to an intermediate anneal gauge, annealed and cold rolled to final gauge.

[0030] Development work for this alloy utilized an apparatus that chilled about 2 to 6 mm thick specimens of the alloy of the present invention from one side at approximately twin roll caster-type cooling rates. These chilled specimens were then machined, from one side, to

make pieces uniform in cross-sectional thickness. Those pieces were then cold rolled to an intermediate gauge (of about 81 microns), annealed for about 1 hour at about 400°C, then cold rolled to about 63 microns for approximating an H14-type temper.

[0031] Table I below lists the compositions of various alloys cast and processed in this manner along with finstock materials included for reference purposes.

Table I
Compositions

Sample	Si	Fe	Cu	Mn	Ni	Zn	In	Ti
Inventive alloys								
1	0.42	2.06	0.14	0.44	0.0	0.63	0.0	0.015
2	0.42	2.02	0.22	0.45	0.0	0.63	0.0	0.015
3	0.43	2.06	0.19	0.45	0.0	0.00	0.0	0.016
4	0.42	2.03	0.16	0.45	0.0	1.66	0.0	0.016
5	0.44	2.00	0.18	0.44	0.0	2.62	0.0	0.016
6	0.42	2.00	0.18	0.43	0.0	0.68	0.0	0.025
7	0.45	2.20	0.20	0.45	0.0	0.75	0.017	0.024
Comparison alloys								
8	0.43	2.11	0.0	0.44	0.0	0.64	0.0	0.014
9	0.44	1.58	0.0	0.48	0.0	0.65	0.0	0.017
10	0.42	1.78	0.0	0.54	0.0	0.66	0.0	0.016
11	0.45	2.00	0.19	0.44	0.0	4.20	0.0	0.016
12	0.91	1.6	0.0	0.62	0.59	0.66	0.0	0.015
13	0.88	1.56	0.0	0.47	0.0	0.64	0.0	0.015
14	0.90	1.81	0.0	0.54	0.0	0.65	0.0	0.015
15	0.6 max	0.7 max	0.05-0.20	1.0-1.5		0.1 max		
16	0.46	1.9	0.02	0.01	1.2	1.2		0.01

[0032] Alloys 1-7 represent the compositions of alloys that are composed by the present invention and alloys 8-16 are the comparison alloys. In particular, alloy 15 represents the composition range for an AA3003 alloy. Alloys 1-5 and 8-14 in Table 1 were processed using laboratory equipment to an H14-type temper, then put through a thermal cycle that simulated a typical CAB braze cycle. That simulation included a 3 minute soak at about 380°C, plus 9 minutes above about 590°C with a peak metal temperature of about 600°C $\pm$ 5°C. Post-braze property assessments included: measuring tensile properties, electrical resistivity (which was then converted to % IACS conductivity values), metallographically measured grain sizes and self-corrosion as measured by weight loss after one week in a neutral salt spray environment per ASTM specification B117, the disclosure of which is incorporated by reference herein. Post braze solution potential was measured in accordance

with ASTM G69 using a saturated calomel electrode but the results were then converted for reference to a saturated AgCl/Ag electrode. The alloy 15 fin from Table 1 was commercially available AA3003 finstock processed from twin roll cast stock. The alloy 16 fin was cast on a high speed belt caster and processed to fin by a combination of hot/warm and cold rolling with an intermediate anneal and cold rolling to final gauge. Both finstocks were then subjected to the same braze cycle simulation and testing as per the other alloys of Table 1.

[0033] In another embodiment, inventive alloys 6 and 7 were cast on a commercial twin roll caster. The alloys were cast at about 5.59 mm thickness. Microstructural evaluation of the cast sheet indicated the casting conditions used did not produce significant amounts of centerline segregation of intermetallic phases. In addition, the formation of coarse primary Fe-bearing intermetallic phases was largely avoided. In the laboratory sections from these as-cast sheets were processed to 50 micron finstock by cold rolling to the intermediate anneal gauge (71 microns), annealing the strips for about 4 hrs. at about 400°C and then cold rolling to 50 microns for an H14 temper.

[0034] The following Table II reports measured post-braze properties of these alloy compositions of Table I.

Table II - Post-Braze Properties

Table II

Alloy	UTS (MPa)	TYS (MPa)	E.C. (% IACS)	Grain Size (microns)	Wt.Loss (mg/sq.cm)	Sol. Potential vs. Ag/AgCl
Inventive alloys						
1	122.7	46.6	50.2	283	0.24	- 703 mV
2	124.6	47.5	49.2	357	0.23	- 699 mV
3	118.6	45.3	50.6	377	0.19	-688 mV
4	122.8	46.2	48.4	423	0.17	-794 mV
5	128.7	54.0	46.8	391	0.32	-860 mV
6	117.2	46.5	50.8	1700		-713 mV
7	121.0	52.4	50.2	1285		-741 mV
Comparison alloys						
8	112.7	44.4	50.1	700	0.20	-723 mV
9	107.5	42.0	50.1	725	0.21	
10	113.2	44.1	49.2	772	0.20	
11	133.8	52.2	44.2	228	0.53	-900 mV
12	139.2	51.3	46.3	238	0.35	
13	125.2	44.6	49.4	950	0.21	- 718 mV
14	126.6	47.7	49.2	840	0.19	- 703 mV
15	111.0	47.6	41.8		0.22	
16	132.2	56.9	52.5	> 10,000	0.97	

[0035] From the foregoing comparisons, it is evident that for inventive alloys 1-7 the post-braze strength and conductivity is markedly improved relative to the alloy 15 fin. Self-

corrosion as measured by weight loss after 1 week in ASTM B117 is comparable with alloy 15. Alloy 5 represents a high Zn level that might be desired in some instances to provide extra cathodic protection to the tube alloy. Zinc clearly has a detrimental influence on the conductivity and increases self-corrosion somewhat. For the comparative alloys low in Fe and essentially free of Cu (alloys 9 and 10), while the post-braze conductivity is significantly higher than alloy 15, the post-braze strength is only comparable to alloy 15. Alloy 8 which had a high Fe content and was essentially free of Cu also demonstrated high conductivity, but strength was comparable to alloy 15. Alloy 11 had a very high Zn content which, while it increases post-braze UTS, (compare to alloy 5), resulted in a markedly low conductivity. Nickel additions, such as used in alloy 12 and the high-Ni alloy 16 yield improved strength with minimal influence on conductivity. However, the self corrosion rate is notably increased.

[0036] Alloys 13 and 14 which are higher in Si content but substantially Cu-free, also exhibited attractive combinations of post-braze properties in comparison to alloy 15. However the alloys of the present invention contain lower Si levels than those alloys and controlled Cu additions for strengthening without resulting in markedly decreased self-corrosion resistance.

[0037] Both alloys 6 and 7 demonstrated good conductivity and higher strength than alloy 15 with acceptable grain size that would minimize sag and erosion tendencies. In addition, it is noted that the combination of Zn and In in alloy 7 was effective in shifting the corrosion potential of the fin to become more anodic with minimal influence on conductivity.

[0038] As noted previously, for ease of fabrication it can be desirable to include an intermediate anneal early in the fabrication sequence. Laboratory work on alloy 7 utilizing various process paths that incorporated two intermediate anneals in the temperature range of 320° - 420°C did not have any notable detrimental influence on post-braze properties. If two intermediate anneals are to be used, it is preferable that some cold work be imparted to the cast sheet prior to the first anneal. Slightly lower post-braze properties are anticipated if the first thermal treatment is imparted to the as-cast sheet prior to cold rolling, but these can still be acceptable properties for some applications. As such the envisioned fabrication paths include routes that have one or two intermediate anneals. The anneal temperatures are preferably in the range of 320°- 450°C for preferably 1 to 8 hrs.

[0039] Control of post-braze grain size is important for high temperature sag resistance. One factor that was found to be very influential in controlling grain size is the amount of final

cold reduction imparted after the last intermediate anneal. Smaller amounts of final cold reduction after the last intermediate anneal resulted in coarser post-braze grain sizes. In laboratory work it was found that final cold reductions of as much as 44% reduction in thickness gave grain sizes in excess of 500 microns for some combinations of composition and fabrication sequences. As such, a final cold reduction of less than 50% is established. Reductions of less than about 35% are preferable.

[0040] While preferred embodiments of the present invention were described hereinabove, modifications and alterations of the present invention may be made without departing from the spirit and scope of the present invention. The scope of the present invention is defined in the appended claims and equivalents thereto.